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Creating biomorphic barbed and branched structures in solution through block copolymer crystallization

Lin Jia,^{1,3,4} Gerald Guerin,^{1,4*} Yijie Lu,¹ Qing Yu,¹ Ian Manners,² and Mitchell A. Winnik^{1*}

¹ Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, ON, M5S 1H6

² School of Chemistry, University of Bristol, Bristol UK, BS8 1TS

³ Laboratory of Polymer Chemistry, Department of Polymer Materials, College of Materials Science and Engineering, Shanghai University, Nanchen Street 333, Shanghai 200444, China.

⁴ These authors contributed equally to this work.

*corresponding authors: gguerin@chem.utoronto.ca, mwinnik@chem.utoronto.ca

Dr. L. Jia, Dr. G. Guerin, Prof. M. A. Winnik
Department of Chemistry, University of Toronto
80 St. George Street Toronto, Ontario, M5S 3H6 (Canada)
Fax: (+1) 416-978-0541
E-mail: mwinnik@chem.utoronto.ca

Prof. I. Manners
School of Chemistry, University of Bristol
Bristol BS8 1TS (United Kingdom)
Fax: (+44) 117-929-0509
E-mail: ian.manners@bristol.ac.uk

ABSTRACT

Branched and barbed structures are common in nature but rare in nanoscale or mesoscale objects formed by bottom-up self-assembly. Key characteristics of the morphology of natural objects such as various types of insects and conifer branches is that they are similar in size and shape, but have unique features such that no two individual objects are exactly the same. Here we report self-assembly conditions for a series of polyferrocenyldimethylsilane-*block*-polyisoprene (PFS-*b*-PI) diblock copolymers that generate biomorphic structures with shapes that depend sensitively on the self-assembly conditions. All of these polymers yield long fiber-like micelles of uniform width with a semicrystalline PFS core in decane. Here we show that injection of a solution of these polymers into THF-decane mixtures, leads to barbed and branched structures of micrometer dimensions, with shapes that depend upon the final THF content of the mixed solvent. These types of structures are not seen with two samples of PFS-*b*-PDMS (PDMS = polydimethylsiloxane) subjected to similar self-assembly conditions. Evaporation of the THF from suspensions of the colloidal biomorphic PFS-*b*-PI structures in the mixed solvents led to rapid rearrangement to elongated fiber-like structures.

INTRODUCTION

Barbed, branched or hairy structures are common in nature. Examples include plant stems, conifer branches and insects, particularly caterpillars and centipedes. The preparation of similarly shaped synthetic structures with dimensions on the scale of nanometers and micrometers is rare. The self-assembly of block copolymers in solution is one approach to produce colloidal structures on this size scale,^[1] but these structures tend to be uniform in shape and lack the structural diversity of natural objects. A rather different set of low curvature structures can be formed by block copolymers with a crystallizable block, particularly when crystallization of the core-forming block drives the self-assembly.^[2-10] In general, the morphologies formed are governed by the competition during crystal growth between the crystallization of the crystalline core-forming block, which favors the growth of the platelets, and the stretching of the corona-forming block, which favors curvature of the core-corona interface.^[11]

The few known examples of biomorphic colloidal mesostructures were prepared by crystallization-driven self-assembly (CDSA) of crystalline-coil block copolymers. PFS-P2VP

(P2VP = poly(2-vinylpyridine)) BCP was used to form sunflower and butterfly-like hybrid silica mesostructures,^[12] while barbed or highly branched structures were generated from the CDSA of P3HT₂₀-*b*-PEG₁₀₈ (P3HT = poly(3-hexylthiophene),^[13] and star-like aggregates were obtained from the hierarchical association of PFS based triblock comicelles.^[14] There was, however, no systematic study of how the sizes and shapes of these structures could be varied through manipulation of the self-assembly conditions.

In this paper, we report the formation of biomorphic wire-like mesostructures in a single step through solvent-induced micellization of polyferrocenyldimethylsilane-*block*-polyisoprene) diblock copolymers. We examine three polymers, PFS₅₀-*b*-PI₁₀₀₀,^[15,16] PFS₆₅-*b*-PI₆₃₇,^[17] and PFS₅₅-*b*-PI₅₀₀ with different block ratios (the subscripts refer to the number of repeat units). Previous studies of crystallization-driven self-assembly of these BCPs led only to the formation of rod-like cylindrical micelles, either in alkane solvents or in mixtures of tetrahydrofuran (THF) and an alkane as a solvent/non-solvent pair.

For the PFS-*b*-PI BCP samples examined here, the solvent composition employed (THF/decane) is similar to that used previously to obtain rod-like micelles,^[16,17] but the sample preparation protocol is different. Slow nucleation in the presence of large amounts of polar solvent led to the formation of highly branched but elongated colloidal objects, often tens of micrometers in length. This represents a new approach to block copolymer self-assembly leading to the spontaneous formation of hierarchical mesostructures.

RESULTS AND DISCUSSION

Self-assembly experiments with PFS-*b*-PI block copolymers normally involve addition of an alkane solvent to a solution of these polymers in THF at room temperature or heating then cooling suspensions of these block copolymer in hexane or decane. When the PI block is longer than the PFS block, these conditions lead exclusively to the formation of elongated micelles uniform in width, and under some conditions, uniform in length as well (c.f., Supporting Information, SI, Figure S1). A number of examples involved PFS₅₀-*b*-PI₁₀₀₀, which we also use in the experiments described below. As shown in Figure 1a, this polymer in decane forms rod-like micelles several μm in length.

The formation of branched superstructures

In contrast to these results, very different types of structures were obtained when aliquots of PFS₅₀-*b*-PI₁₀₀₀ in THF (10 μ L, c = 10 mg/mL) were added to vials containing different mixtures of decane and THF, leading to final polymer concentrations c_{BCP} = 0.4 mg/mL (see Table S1). Each sample was sealed, swirled, and allowed to stand one day before a TEM grid was prepared. For a sample in which the final solvent composition was 10.7 vol % THF, we obtained the interesting structures seen in Figure 1b-d. The overall length of these branched structures was on the order of 20 μ m. They are characterized by a darker central core with densely packed fiber-like protrusions. Higher magnification images of this hairy corona suggest that the fibers are wider and more ribbon-like than the rod-like micelles formed in decane as seen in Figure 1a. The average length of these fiber-like structures protruding from the backbone was ca. 6 μ m. It is striking how much these structures resemble the caterpillar shown in Figure 1e, characterized by tufts of hairy protrusions from a central body. For convenience, we will refer to this type of structure as a "hairy supermicelle".

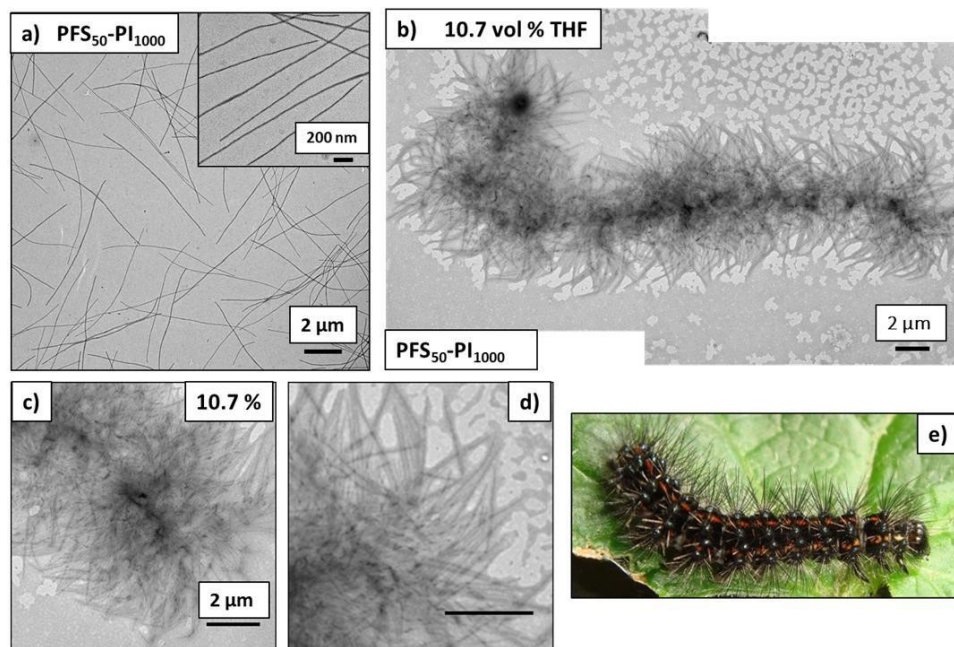


Figure 1. TEM images of representative structures formed by PFS₅₀-*b*-PI₁₀₀₀ at 0.4 mg/mL, **a)** The polymer was dispersed in decane, heated at 90 °C, then aged at room temperature for 24 h. **(b)** The polymer was dissolved in THF, added to a decane-THF mixture with a final THF content of 10.7 vol %, then aged 24 h. **c), d)** higher magnification images of other hairy supermicelles on the grid. **e)** Photographic image of a magpie moth caterpillar (<http://www.terrain.net.nz/friends-of-te-henui-group/caterpillars/caterpillar-of-the-magpie-moth-nyxctemera-annulata.html>).

To explore the effect of THF on the formation of these structures, we performed analogous experiments in which the polymer concentration was fixed and THF content was varied (c.f., Table S1). After allowing the solutions to stand one day, samples were placed on grids and imaged by TEM. At low THF content (3.8 vol %, Figure 2c,d; 5.6 vol %, Figure 2e,f), the structures resemble barbed wire grass or the branches of a conifer. The backbone strands are extremely long, and it is difficult to distinguish the beginning and the ends of these structures. At higher magnification (Figure 2d,f), the backbone strands appear to consist of either rigid fibers aligned side-by-side, or flat ribbons, and in the lower part of Figure 2d, one can see where a ribbon has folded as it deposited on the grid. At a somewhat higher THF content (7.4 vol %), a mixture of barbed ribbons and branched micelles formed (Figure 2g,h). At this THF content, the micelles appear to consist of a central core of aligned fibers with needle-like micelles extending radially from the central backbone. The average length of these protruding fibers was ca. 3 μm . The higher magnification image in Figure 2h indicates that these protrusions are flattened compared to the micelles formed in decane. One sees that for each set of self-assembly conditions, one obtains objects that are similar in form. As with species present in nature (Figure 2a,b), one also finds structural diversity within each set of objects in that each individual object is different.

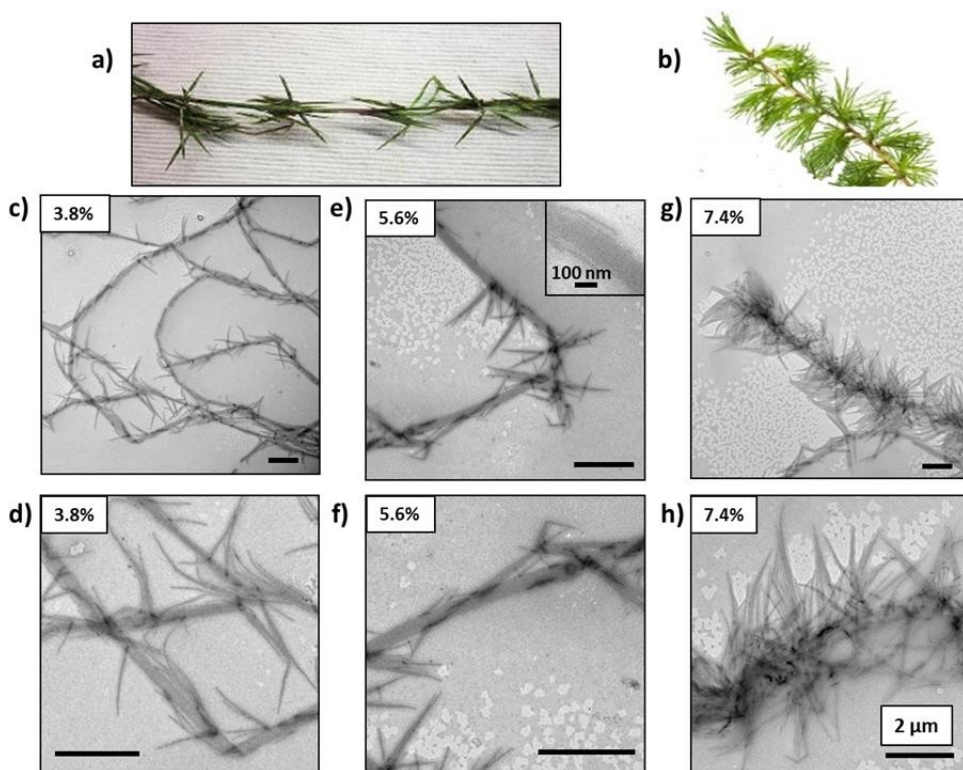


Figure 2. Photographic images of a) a strand of barbed-wire grass (<http://tomandannes-garden.blogspot.ca/2012/03/barbed-wire-grass.html>), and b) a branch of a European Larch (<http://www.abtreegene.com/trees.html>). TEM images of representative structures formed by PFS₅₀-*b*-PI₁₀₀₀ at 0.4 mg/mL in decane-THF mixtures containing c), d) 3.8 vol% THF, e), f) 5.6 vol% THF, g), h) 7.4 vol% THF. d), f), h) Higher magnification images of the structures formed. The scale bars are 2 μ m.

To test the scope of this unusual self-assembly from PFS-*b*-PI copolymers that normally form uniform fiber-like micelles,^[17] we examined PFS₆₅-*b*-PI₆₃₇, and PFS₅₅-*b*-PI₅₀₀, which have smaller block ratios (ca. 1:10) than PFS₅₀-*b*-PI₁₀₀₀. TEM images of the structures obtained with PFS₆₅-*b*-PI₆₃₇ are presented in Figure 3. At 3.8 vol % THF (Figure 3a), we found kinked ribbons with a few fibers protruding from the backbone. At both 5.6 and 7.4 vol % THF, the TEM images show networks consisting of ribbons and fibers. At the highest THF content (10.7 vol %, Figure 3d), we found structures resembling the hairy supermicelles obtained with PFS₅₀-*b*-PI₁₀₀₀ in decane/THF mixtures at 7.4 and 10.7 vol % THF. Examples of branched structures formed by PFS₅₅-*b*-PI₅₀₀ at 10.7 vol% THF are shown in Figure S2.

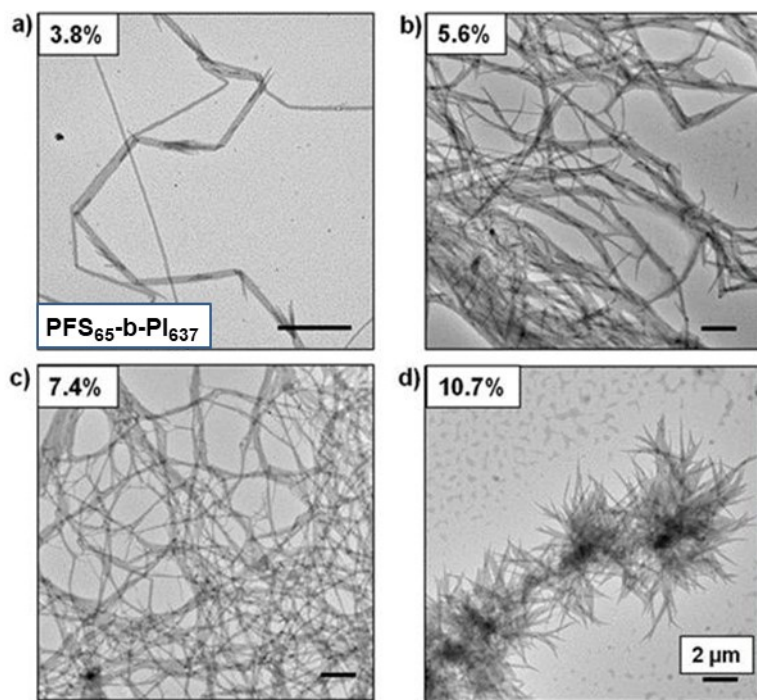


Figure 3. Representative structures formed by PFS₆₅-*b*-PI₆₃₇ at 0.4 mg mL⁻¹ in THF/decaane mixtures with the THF content of the solution, in vol %, indicated in each panel. Identical amounts of polymer in THF were added to vials containing decaane or decaane-THF mixtures. The scale bars are 2 μ m.

In contrast, this self-assembly protocol only led to the formation of very long ($> 10 \mu$ m) fiber-like micelles of uniform width (cf. Figures S3, S4) when PFS-*b*-PDMS (PDMS = polydimethylsiloxane) BCPs were used instead of PFS-*b*-PI.

Time profile and mechanism of structure formation

Multiangle light scattering (LS) measurements (Figure S5) of a freshly prepared solution of PFS₆₅-*b*-PI₆₃₇ at 0.4 mg mL⁻¹ in THF/decane (10.7% THF) showed that it only contained molecularly dissolved polymer (unimer). Up to 1h, there was no significant increase in the scattering intensity (Figure S6), but at later times there were spikes in the scattering signal that were visible by eye. These results indicate that the onset of association was slow, but led to the formation of large aggregates or assemblies that scattered light intensely when they passed through the laser beam of the LS instrument.

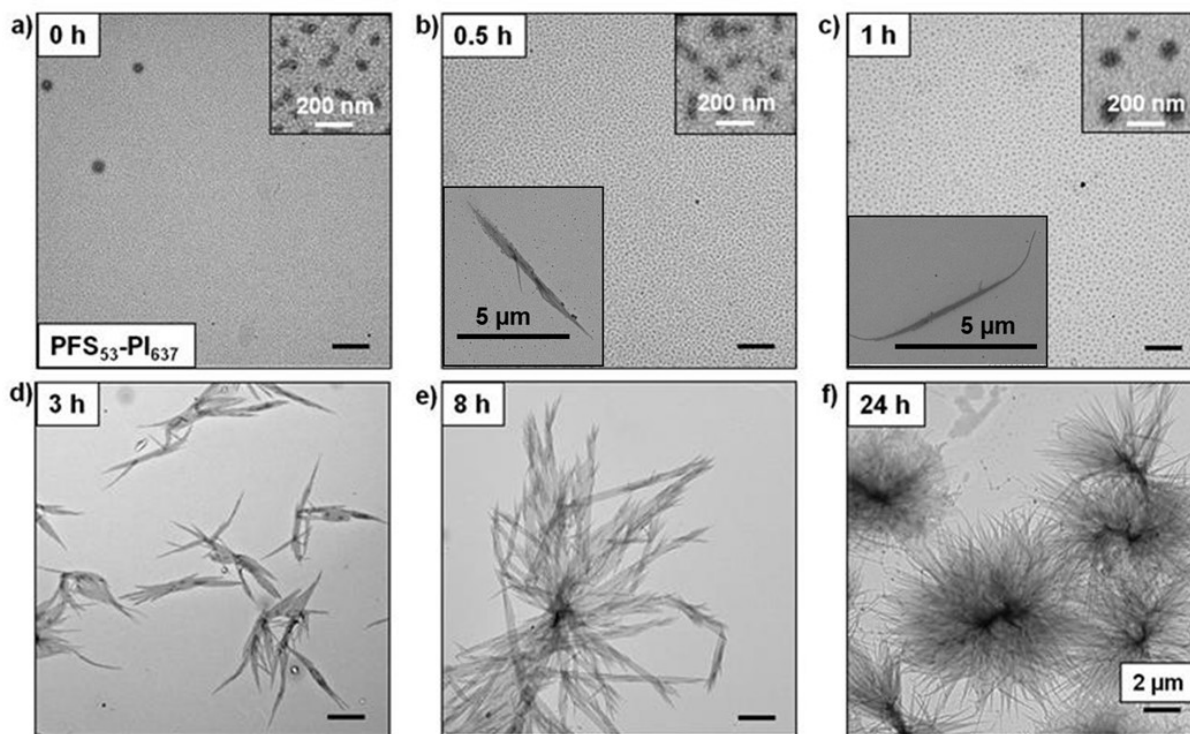


Figure 4. TEM images of the micelles formed by PFS₆₅-*b*-PI₆₃₇ at 0.4 mg/mL in a decane-THF mixture containing 10.7 vol % of THF. A drop of solution was taken out of the solution at different incubation times: (a) 0 h, (b) 0.5 h, (c) 1 h, (d) 3 h, (e) 8 h, (f) 24 h. Space bars are 2 μm, except in the insets. The insets for 0.5 h and 1 h are from a different set of experiments (see Figure S4) in which we found very occasional and larger objects on the grid.

Parallel kinetics experiments were also performed to study the structure formation by TEM (Figure 4a-c). At early times, we found only small amorphous structures, approximately 10 to 20 nm in width, that presumably formed from unimer as the solvent evaporated. At 3 h (Figure 4d), we note the appearance of branched structures, with dimensions on the order of 5 to 10 μm. As seen in Figures 4e,f, these assemblies grew in size and complexity over time. Similar results were obtained for PFS₅₀-*b*-PI₁₀₀₀ (Figure S7). Taken together, these results point to a nucleation

and growth mechanism in which rare nucleation events at this polymer concentration lead to the formation of large elongated assemblies.

The important mechanistic questions are i) how are these structures formed and ii) how do they grow? Experiments with PFS₆₅-*b*-PI₆₃₇ (0.4 mg mL⁻¹ in decane/THF, 10.7%) were repeated many times. In one set of experiments (see SI and Figures S8-S10 for details), we found occasional elongated lenticular objects on the grid for samples taken 30 min and 1 h after sample preparation. An example of each is shown as insets in Figure 4b,c. These objects were present in such small numbers that they did not contribute to the light scattering signal at times up to 1 h. We presume that these are the earliest assemblies formed following homogeneous nucleation in the solutions. While local growth of assemblies following nucleation may be rapid, overall growth is slow. As seen in Figure S10, even after 8 h, one can see spots due to amorphous aggregates on the TEM grid along with branched micelles. This observation leads us to conclude that a significant unimer population persists in these solutions over many hours.

We were surprised to see the ribbon-like shapes in the TEM images presented in Figures 2 – 4). In micelles formed by PFS block copolymers with long corona-forming blocks such as the three PFS-*b*-PI BCPs examined here, the width of the micelle is normally limited by corona chain repulsion that suppresses growth of incoming unimer on the lateral faces of the micelle. Elongated planar assemblies are normally observed only for PFS block copolymers with short corona-forming chains.^[3,4]

We have previously reported that polar solvents can promote the formation of planar assemblies. For example, in 2-propanol PFS₇₅-*b*-P2VP₄₅₄, PFS₁₀₂-*b*-P2VP₆₂₅ (P2VP = poly(2-vinylpyridine)) formed spherical micelles or mixtures of spheres and a few rods. Addition of THF to these solutions to enhance the solubility of the PFS led to the formation of crystalline rod-like micelles as well as long thin planar polycrystalline (lenticular) micelles.^[18] We also found the initial formation of ribbon-like micelles upon cooling hot solutions of PFS₅₀-*b*-PI₁₀₀₀ in tert-butyl acetate (*t*BA),^[19] a better solvent for PFS than decane (see Table S2 for solubility parameters). In both examples, we proposed that swelling of the PFS core in the micelles enhanced lateral growth of the core as a consequence of reduced repulsion among the corona chains, leading to ribbon-like, rather than rod-like structures. Corona repulsion is also affected by solvent quality. Decane is a poor solvent for PFS but a better solvent for PI than THF (Table S2). From this perspective, we expect that solvent mixtures lean in THF will lead to less swelling of

the PFS core, greater swelling of the PI corona, and a more pronounced tendency to form rod-like, rather than ribbon-like structures. This concept provides a convenient explanation of why solvent mixtures containing smaller amounts of THF (3.8, 5.6, 7.4 vol%) promote formation of narrower barbed wire-like structures. It also suggests an explanation for the absence of branched micelle aggregates for the two PFS-*b*-PDMS samples. Decane is a very good solvent for PDMS. Corona-chain swelling in decane-rich media for these PFS-*b*-PDMS samples suppresses branching, yielding elongated micelles of uniform width.

Structure evolution upon removal of THF

Rod-like PFS-*b*-PI micelles are kinetically frozen in decane at room temperature. Samples of micelles of uniform length preserve their length and width for months when stored in sealed containers. In the presence of THF, the micelle structure may be more dynamic because THF can plasticize the PFS core. As a consequence, we examined whether the structures formed by these PFS-*b*-PI BCPs would persist as the THF was removed by evaporation.

To carry out this experiment, we began with a solution of PFS₅₀-*b*-PI₁₀₀₀ hairy supermicelles similar to that shown in Figure 1b (see Figure 5a,b) in a decane/THF mixture (0.4 mg mL⁻¹ in decane/THF, 10.7%). To evaporate the THF, we used a rotary evaporator (water bath at 5 °C, ca. 150 mbar, and 90 rpm rotation rate). In Figure 5, one sees that the system was dynamic. The TEM image in Figure 5c taken after partial removal of the THF showed a transformation from the caterpillar-like structures present initially to barbed-wire like structures similar to those formed at 4 vol % THF seen in Figure 2c. After 2 h, when essentially all the THF was removed (c.f., Figure S11), no branched micelles remained. As shown in Figure 5d, we found a dense array of extremely long fiber-like micelles. Similarly, we found that the branched micelles formed by PFS₅₀-*b*-PI₁₀₀₀ at 7.4 vol% THF (Figures 2g and S12a), and branched micelles formed by PFS₆₅-*b*-PI₆₃₇ at 10.7 vol% THF (Figures 5f and S13a-c) also reorganized to form isolated long cylindrical micelles (Figures S12b, S13c,d, respectively) as the THF was removed from the solution. These experiments indicate that during THF evaporation the system rearranged from hairy supermicelles to long branched structures and finally to elongated linear micelles.

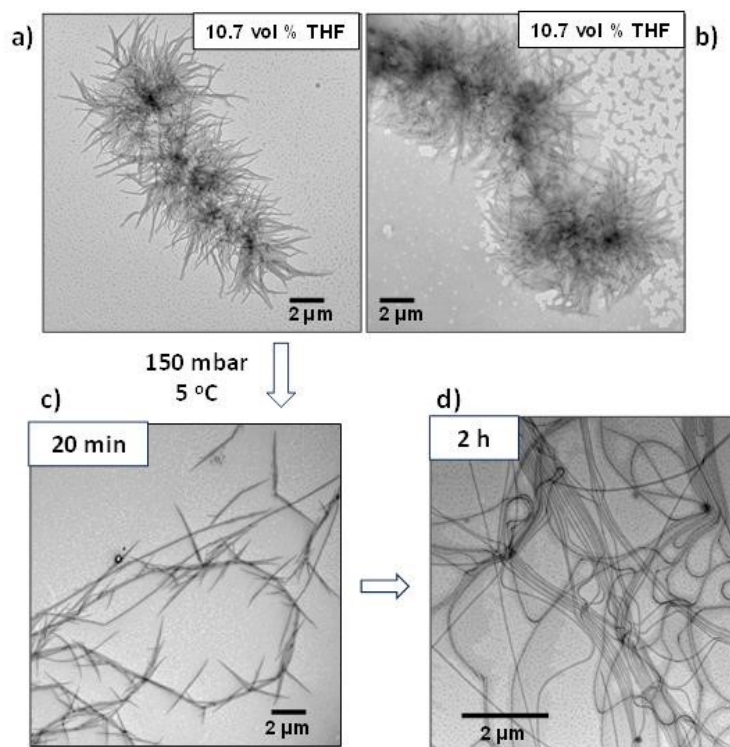


Figure 5. TEM images of (a) hairy supermicelles formed by PFS₅₀-*b*-PI₁₀₀₀ in a 10.7 vol % THF-decane mixture. To reduce the THF content of the solution, the vial containing the solution of branched micelles was subjected to mild rotary evaporation for c) 20 min and d) 2 h. Scale bars are 2 μm.

The morphology rearrangement is consistent with the idea that uniform rods represent the thermodynamically favored self-assembly state for core-crystalline PFS-*b*-PI micelles in which the PI block is significantly longer than the PFS block. What remains surprising to us is how rapidly this transformation took place. The aspect the morphology transformation most in need of further investigation is the disassembly mechanism that precedes micelle growth.

SUMMARY

In this paper we show that three PFS-*b*-PI block copolymers that normally form rod-like core-crystalline micelles in decane or decane/THF mixtures will form highly branched biomorphic structures, tens of μm in overall length, under a specific set of sample preparation conditions. These conditions involve addition of the block copolymer as a solution in THF to a THF/decane mixture in which the final polymer concentration is 0.4 mg/mL. The concentration of BCP in the THF solution plays an important role. At lower final THF contents (3.8, 5.6 vol %) in the final mixture, open barbed structures that resemble “barbed-wire grass” are formed, whereas at higher THF contents (e.g., 10.7 vol %) insect-like hairy supermicelles are formed. As

such, this represents a new protocol for crystallization-driven self-assembly that opens the door to new and more complex hierarchical structures.

When the THF is removed from solutions of these branched supermicelles the micelles rearrange to form very long linear structures indistinguishable from those formed by heating and cooling in decane. Many more experiments are needed, particularly on the kinetics of structure evolution, in order to understand the mechanism of these remarkable morphology transformations.

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SUPPORTING INFORMATION

Supporting information for this article is available on the WWW under <http://...>

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